

Supporting information for

“An Excellent BODIPY Dye Containing Benzo[2,1,3]thiadiazole Bridge as Highly Selective Colorimetric and Fluorescent Probe for Hg²⁺ with Naked-eye Detection”

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General

^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded at room temperature using TMS as an internal standard on Bruker Ultra Shield Plus 400 MHz instrument. The chemical shifts (δ ppm) are referenced to the respective solvents and splitting patterns are designed as s (singlet), d (doublet) and m (multiplet). The mass spectra were obtained on a Bruker autoflex MALDI-TOF/TOF mass spectrometer. The column chromatography was carried out using silica gel (200-300 mesh). The TLC analysis was carried out on single coated silica glass plates. All the solvents and metal salts were used as received.

Spectrophotometric titrations were performed on 10 μM solutions of **3** in CH_2Cl_2 for both Uv-vis absorption and PL spectra. 2.5 mL solution was added into quartz cuvette, then the Uv-vis absorption and PL spectra of samples were recorded upon the addition of aliquots of fresh Mercury (II) in CH_3CN , respectively. Furthermore, other ten kinds of cations (magnesium(II), argentum(I), nickel(II), cobalt(II), iron(III), copper(II), lead(II), cadmium(II), chromium(II) and zinc(II), were also investigated. For other metal ions except mercury(II,) were tested for selectivity using the same methods.

Cyclic voltammetry: The experiments were conducted in anhydrous acetonitrile under a nitrogen atmosphere, at room temperature. The potentials are reported vs ferrocene as internal standard using a scan rate of 100 mV s^{-1} , Ag/AgNO₃ reference electrode, platinum counterelectrode, and 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte.

Uv-vis titration method

The PL spectroscopic titrations of **3** with Hg^{2+} was carried out in CH_2Cl_2 . A sensor solution was titrated by adding a solution of Hg^{2+} . The resulting decrease in intensity was fit using eq 1, as described by Zhao.¹

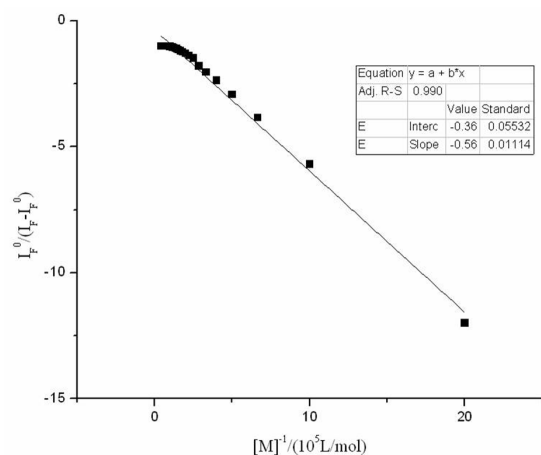
$$I_F^0/(I_F - I_F^0) = [a/(b-a)][(1/K[M])+1] \quad 1$$

I_F^0 = emission intensity of **3** at 603 nm.

I_F = emission intensity of **3** at 603 nm upon the addition of different amount of Hg^{2+} .

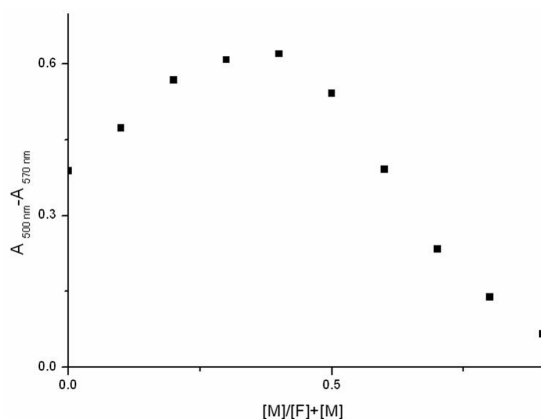
$[M]$ = concentration of Hg^{2+} .

The association constant values K is given by the ratio intercept/slope.



Job's method

Job's Plot had be used to further confirme the stoichiometry of the host-guest complex. The **3** and Hg^{2+} was dissolved in CH_2Cl_2 and CH_3CN resectively at appropriate concentrations, which were then mixed and diluted with the solvent to control the concentrations. The sun of the total concentration of **3** and Hg^{2+} namely $[\text{F}]+[\text{M}]$ was maintained to be constant. At the same time, the ratio $[\text{F}]/[\text{M}]$ was varied from 1:9 to 9:1. After recording the UV-visible spectrum of these solutions, the appropriate absorbance values were plotted against the mole fraction of the Hg^{2+} . The appearance of maximum near 0.5 confirmed the 1:1 stoichiometry between **3** and Hg^{2+} .



Theoretical calculations

The structure optimization of model compound of **3** was performed with the Gaussian 03 package using B3LYP density functional theory (DFT). The 6-31G(d) basis set was used to treat all atoms. To reduce the calculation, the alkyl-chains was substituted by methoxyl. The contours of the HOMO and LUMO orbitals were plotted. On the basis of ground- and excited-state optimization, the time-dependent density functional theory approach was applied to predict their absorption and emission properties. The solvent effect (CH_2Cl_2) was simulated using the polarizable continuum model (PCM) in which the solvent cavity is regarded as a union of interlocking atomic spheres.

Synthetic experimental

4,7-Diethynylbenzo[c][1,2,5]thiadiazole was synthesized according to the literature procedures.²

4-(Octyloxy)benzaldehyde

When 120 mL of degassed acetone was added to a 500 mL three-neck round-bottom flask containing 4-hydroxylbezaldehyde (5.0 g, 41 mmol), 1-bromooctane (9.8 g, 51.25 mmol), and K_2CO_3 (20.0 g, 144 mmol) under a nitrogen atmosphere, the mixture was stirred for overnight in reflux condition. After completion of the reaction (which was monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was dissolved in 50 mL of EtOAc and washed twice with water and saturated NaCl solution. The organic layer was collected, dried over anhydrous Na_2CO_3 , and concentrated under reduced

pressured. The resulting crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (30/1, v/v) to obtain white solid (6.5 g, 67.6%). ¹H NMR (400 MHz, CDCl₃): δ = 9.84 (s, 1H), 7.79 (d, J = 8.6Hz, 2H), 6.95 (d, J = 8.6Hz, 2H), 4.0 (m, 2H), 1.78 (m, 2H), 1.48-1.21 (m, 10H), 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 190.66, 164.25, 131.93, 129.74, 114.71, 68.39, 31.79, 29.31, 29.21, 29.05, 25.96, 22.65, 14.08 ppm.

4,4-Difluoro-8-(4-octyloxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BDP)

4-(Octyloxy)benzaldehyde (0.70 g, 3.0 mmol) and 2,4-dimethylpyrrole (0.63 g, 6.6 mmol) were dissolved in dry THF (90 mL) under a nitrogen atmosphere. Three drops of trifluoroacetic acid (TFA) (about 0.2 mL) were added, and the mixture was stirred at room temperature overnight. After TLC monitoring showed complete disappearance of the aldehyde, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.68 g, 3.0 mmol) in anhydrous THF (120 mL) was added. This mixture was further stirred for 3h, then 18 mL of Et₃N and 18 mL of BF₃·OEt₂ were successively added and after reacting overnight, the reaction mixture was washed thoroughly with water and brine, dried over anhydrous Na₂CO₃, filtered, and evaporated under vacuum. The crude compound was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate: from first 30:1 to final 10:1, increasing the polarity of the solvent) to give a shiny orange powder (0.85g, 62.6%). ¹H NMR (400 MHz, CDCl₃): δ = 7.15 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 5.97 (s, 2H), 4.00 (m, 2H), 2.55 (s, 6H), 1.82 (m, 2H), 1.46-1.53 (m, 2H), 1.43 (s, 6H), 1.26-1.40 (m, 8H), 0.90 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.73, 155.20, 143.19, 142.02, 131.87, 129.14, 126.80, 121.07, 115.07, 77.36, 77.04, 76.72, 68.18, 31.83, 29.42, 29.27, 29.25, 26.08, 22.68, 14.59, 14.12 ppm.

4,4-Difluoro-8-(4-octyloxyphenyl)-2-iodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1)

BDP (452 mg, 1 mmol), iodine (158 mg, 1.25 mmol) and EtOH (30 mL) were added to a 100 mL round-bottomed flask and to this solution was added iodic acid (176 mg, 1.25 mmol) dissolved in 1 mL of water. The reaction mixture was stirred at 60 °C and was monitored by TLC. When all the starting material had been consumed, saturated Na₂S₂O₃ solution in water was added and the product was extracted into CH₂Cl₂. The solvent was evaporated and the residue was purified by neutral alumina column chromatography using petroleum ether/ethyl acetate (100/1, v/v) to obtain wine solid (266 mg, 46%). ¹H NMR (400 MHz, CDCl₃): δ = 7.11 (d, J = 8.5Hz, 2H), 7.00 (d, J = 8.5Hz, 2H), 6.03 (s, 1H), 4.01 (m, 2H), 2.63 (s, 3H), 2.55 (s, 3H), 1.83 (m, 2H), 1.54-1.46 (m, 2H), 1.44 (s, 3H), 1.43 (s, 3H), 1.40-1.27 (m, 8H), 0.90 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.95, 157.56, 154.22, 145.27, 143.25, 141.86, 132.32, 131.39, 129.08, 126.55, 122.19, 115.25, 84.13, 68.23, 31.84, 29.43, 29.27, 26.09, 22.70, 16.87, 15.78, 14.85, 14.78, 14.16 ppm.

4,4-Difluoro-8-(4-octyloxyphenyl)-2-ethynyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2)

BODIPY Dye **1** (400 mg, 0.69 mmol), CuI (6 mg, 0.03 mmol), and Pd(PPh₃)₄ (40 mg, 0.035 mmol) were added to a three-neck round-bottom flask under a nitrogen atmosphere. When 10 mL of anhydrous degassed THF, 10 mL of anhydrous diisopropylamine, and trimethylsilylacetylene (82 mg, 0.84 mmol) were added to the flask, the mixture was stirred under reflux for 4h. After the completion of the reagent (which was monitored by TLC), the reaction mixture was concentrated and dissolved in 50 mL of CH₂Cl₂ and washed twice with water and saturated saline solution. The organic layer was collected, dried over anhydrous Na₂CO₃, and concentrated under reduced pressure. The product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (30/1, v/v) to yield orange-red solid. Then this solid was dissolved in 10 mL CH₂Cl₂ under a nitrogen atmosphere. When 10 mL of methanol solution of sodium hydroxide (400 mg, 10 mmol) was successively added, the mixture was stirred for 30 min at R.T. Then the reaction was finished by extracting with water and dichloromethane 3 times. The organic layer was dried with anhydrous Na₂CO₃ and evaporated under reduced pressure. The product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (30/1, v/v) to yield red solid (287 mg, 86%). ¹H NMR (400 MHz, CDCl₃): δ = 7.13 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.03 (s, 1H), 4.01 (t, J = 6.6 Hz, 2H), 3.28 (s, 1H), 2.63 (s, 3H), 2.56 (s, 3H), 1.96-1.69 (m, 2H), 1.51 (s, 3H), 1.45 (s, 3H), 0.90 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.92, 157.85, 156.34, 145.10, 143.67, 142.65, 133.05, 130.29, 129.05, 126.34, 122.15, 115.21, 113.77, 83.29, 77.35, 77.04, 76.72, 76.55, 68.22, 31.82, 29.41, 29.25, 26.07, 22.67, 14.80, 14.77, 14.12, 13.31, 13.23, 1.03 ppm.

Dye 3

1 (100 mg, 0.16 mmol) was dissolved in 10 mL freshly distilled THF and 5 mL (i-Pr)₂NH. Then the reaction was purged with nitrogen until all the chemicals were added. After 15 minutes Pd(PPh₃)₄ (16 mg, 0.014 mmol) and CuI (3 mg, 0.014 mmol) were added to the reaction mixture. Then 4,7-diethynylbenzo[c][1,2,5]thiadiazole (11 mg, 0.06 mmol) was added after 10 minutes. The stirring was continued 12 hours at 60°C. The reaction mixture was evaporated under reduced pressure and the compound was purified over silica gel using chloroform/petroleum ether (3/1, v/v) as a red solid 27 mg in 42% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (s, 2H), 7.17 (d, J = 8.6 Hz, 4H), 7.02 (d, J = 8.6 Hz, 4H), 6.04 (s, 2H), 4.02 (t, J = 6.6 Hz, 4H), 2.78 (s, 6H), 2.58 (s, 6H), 1.89-1.74 (m, 4H), 1.64 (s, 6H), 1.46 (s, 4H), 0.90 (t, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.96, 158.05, 156.46, 154.32, 145.22, 143.07, 142.55, 133.19, 131.07, 130.79, 129.10, 126.33, 122.28, 116.88, 115.21, 114.47, 92.37, 90.94, 77.35, 77.23, 77.03, 76.71, 68.23, 31.83, 29.71, 29.42, 29.26, 29.25, 26.08, 22.68, 14.83, 14.13, 13.52 ppm; MS (MALDI-TOF) (m/z): 1084.569.

Dye 4

The product was synthesized according to the literature procedures³ ¹H NMR (400 MHz, CDCl₃): δ = 7.12 (d, J = 8.6 Hz, 4H), 7.00 (d, J = 8.6 Hz, 4H), 6.04 (s, 2H), 4.01 (t, J = 6.6 Hz, 4H), 2.64 (s, 6H), 2.56 (s, 6H), 1.97-1.68 (m, 4H), 1.51 (s, 6H), 1.45 (s, 6H), 0.90 (t, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.95, 158.35, 157.33, 145.43, 143.95, 142.53, 133.34, 130.30, 129.03, 126.19, 122.39, 115.24, 113.58, 80.11, 77.36, 77.24, 77.04, 76.72, 75.60, 68.23, 31.82, 29.41, 29.25, 26.07, 22.67, 14.84, 14.12, 13.60, 13.42 ppm.

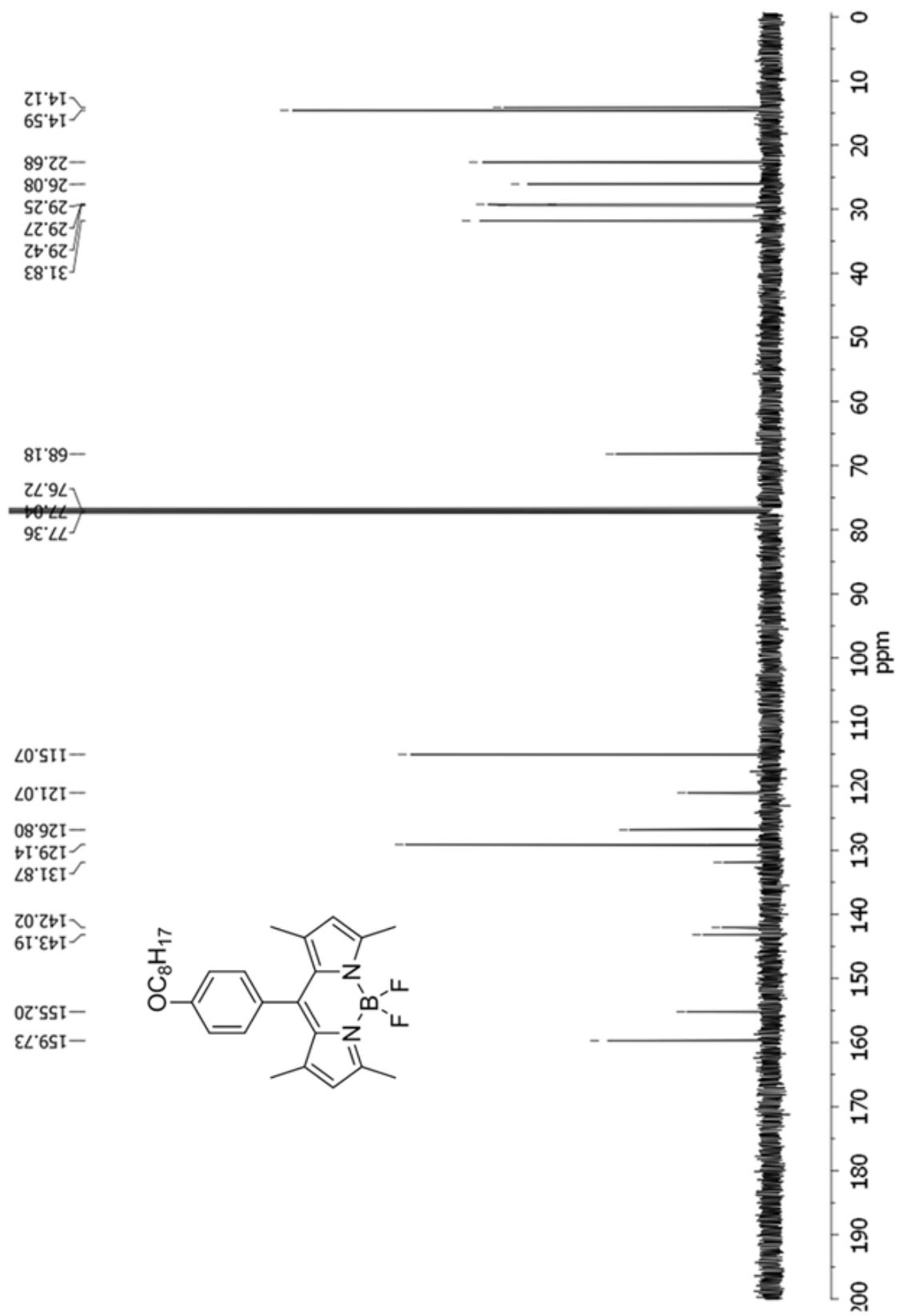


Figure S2. ^{13}C NMR spectrum of BDP

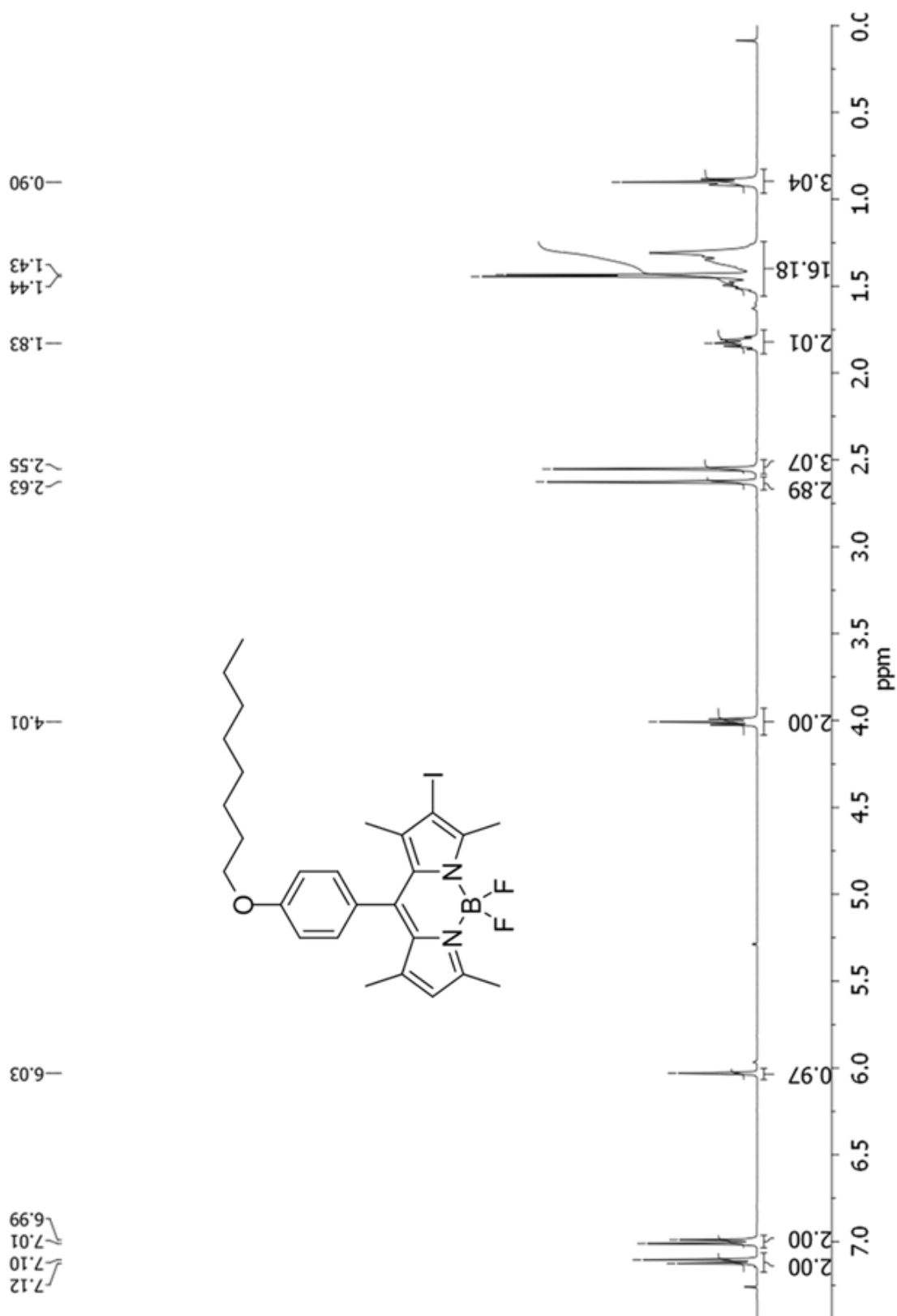


Figure S3. ¹H NMR spectrum of 1

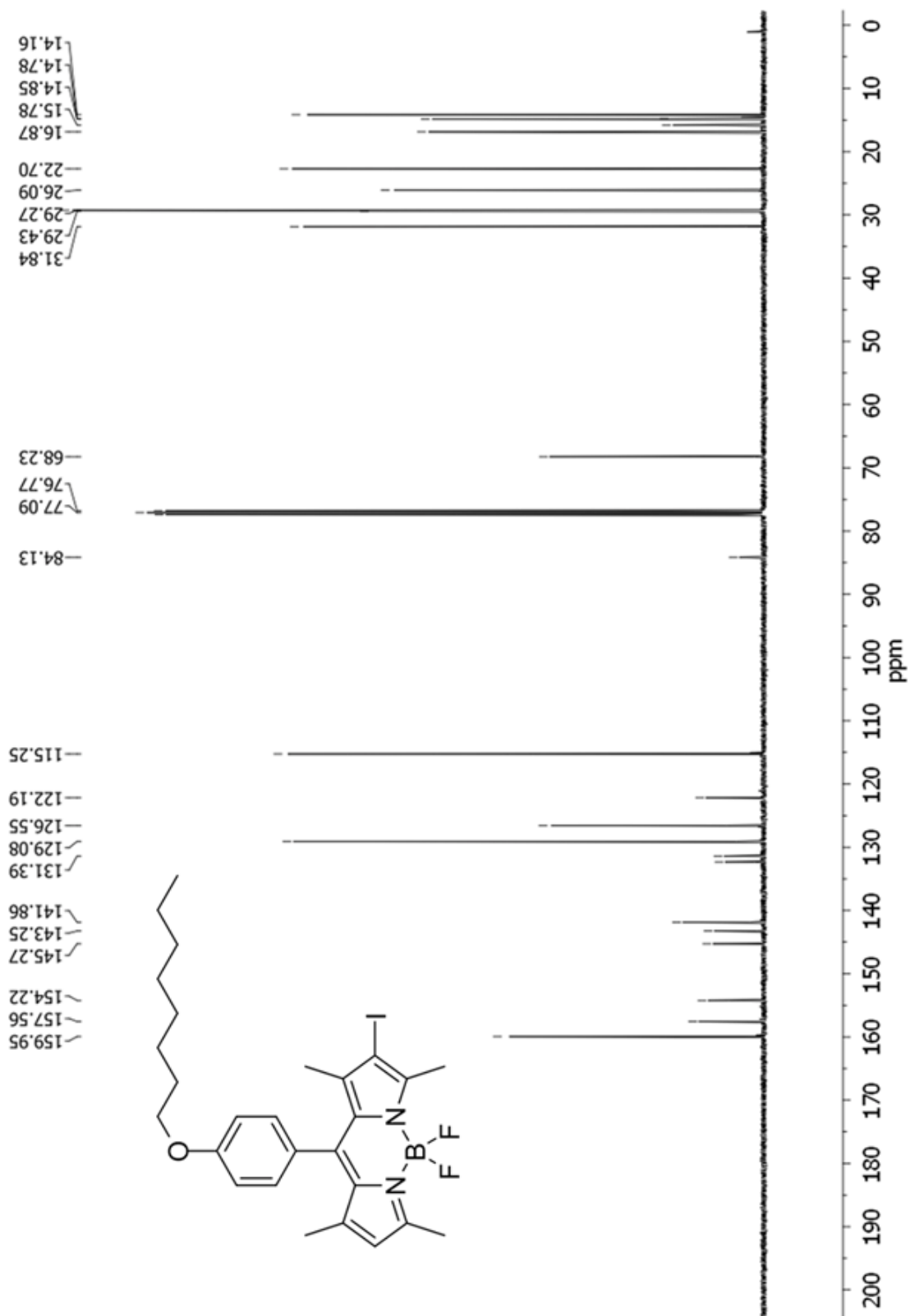


Figure S4. ¹³C NMR spectrum of 1

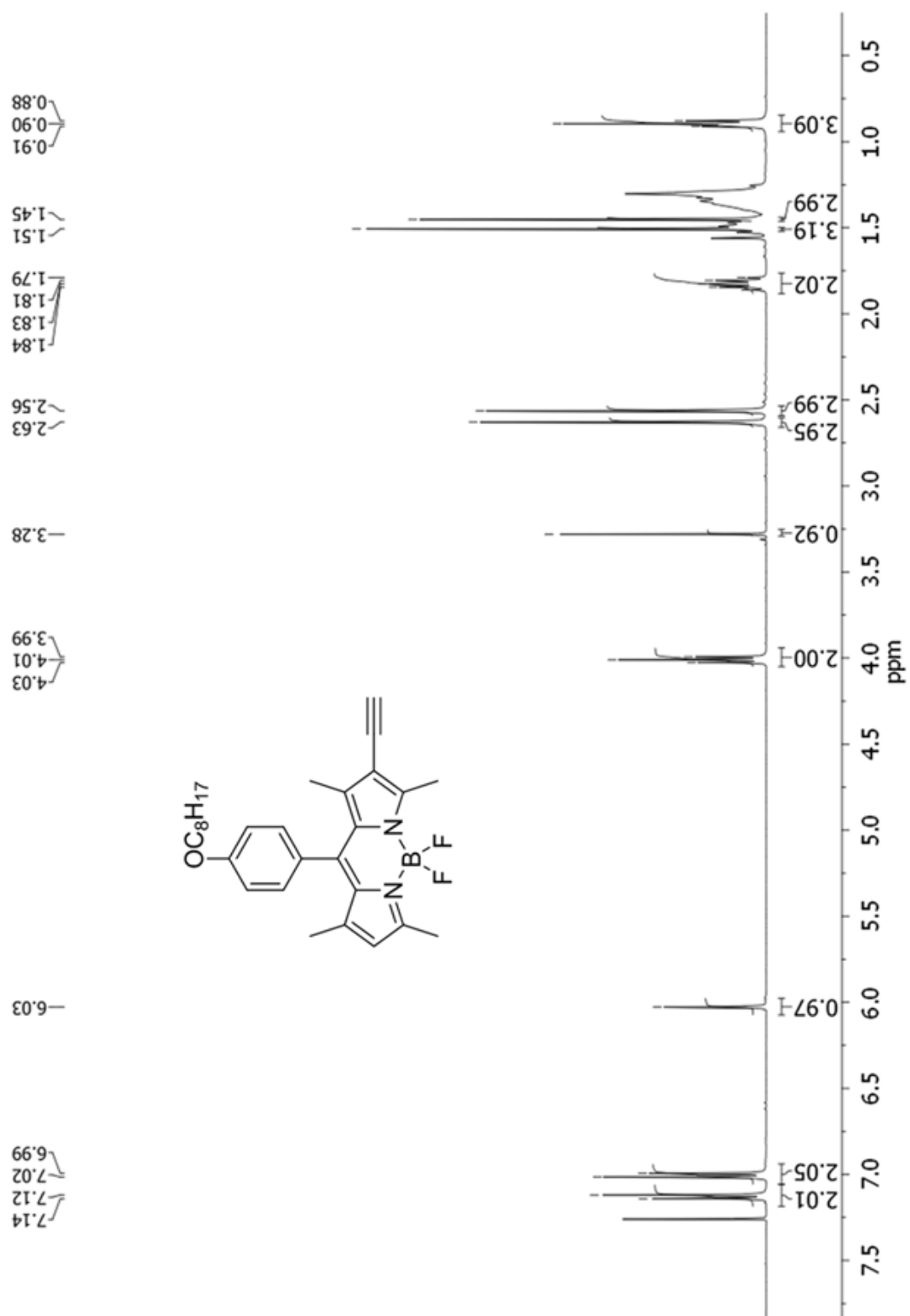


Figure S5. ^1H NMR spectrum of 2

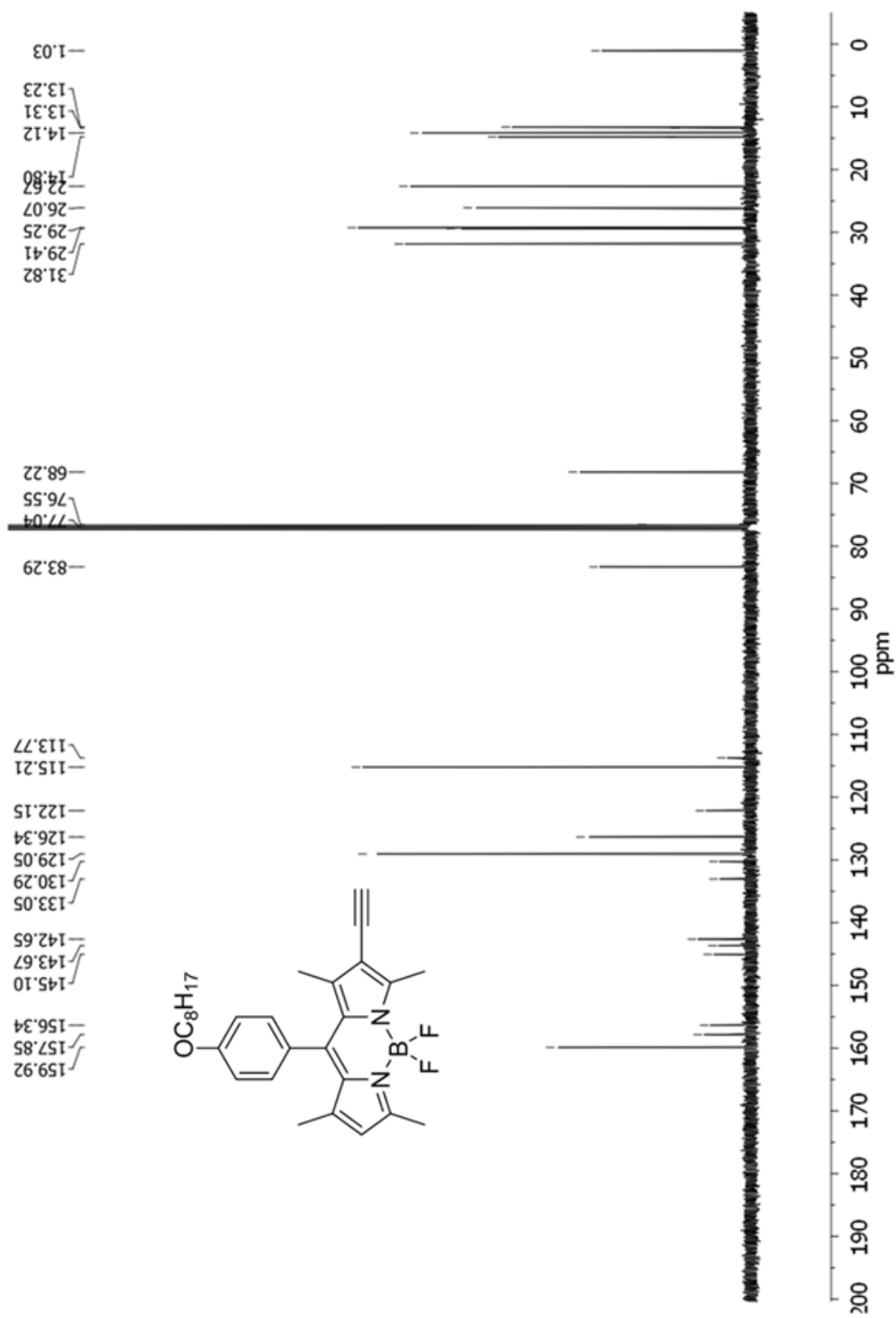


Figure S6. ^{13}C NMR spectrum of 2

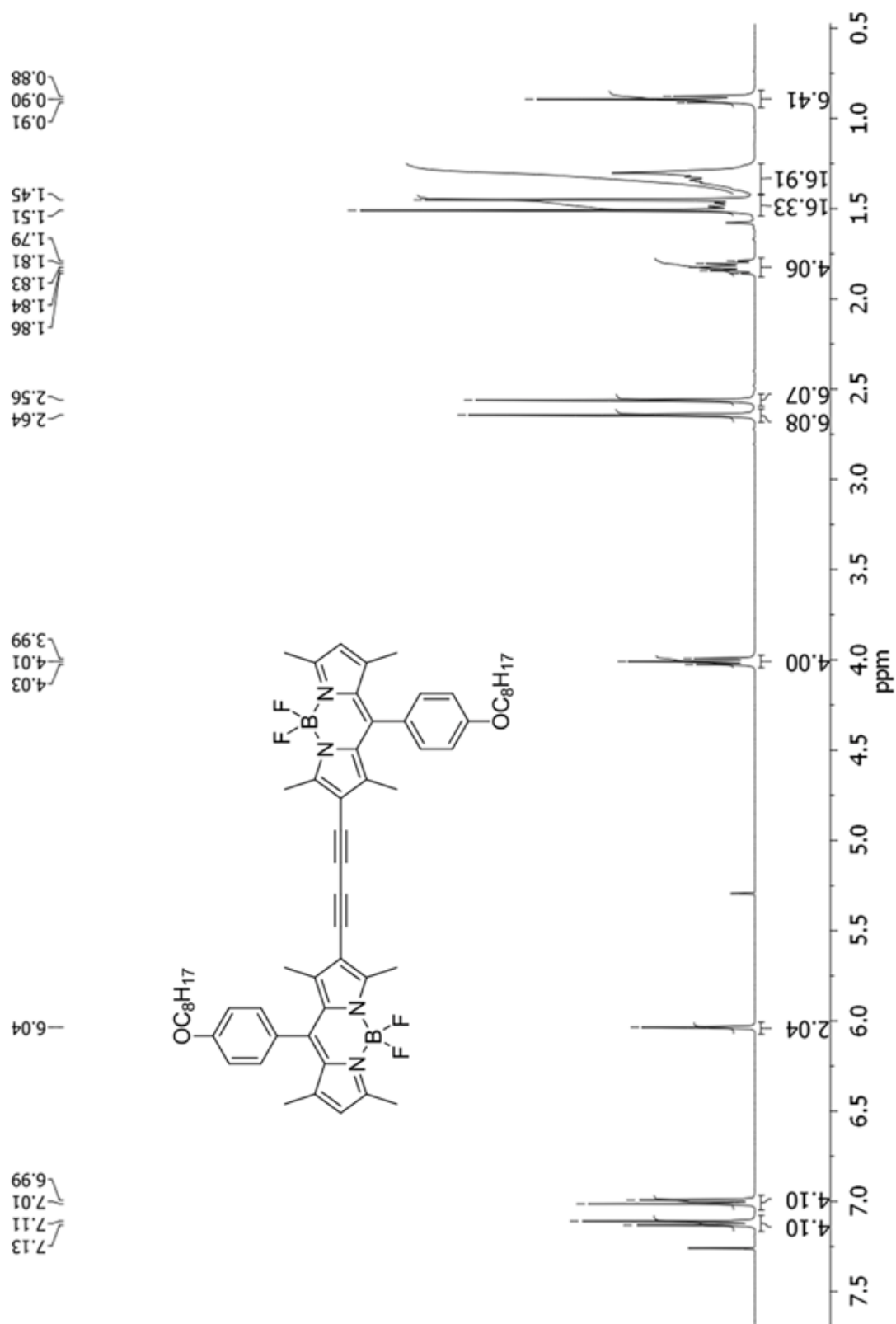


Figure S7. ¹H NMR spectrum of 4

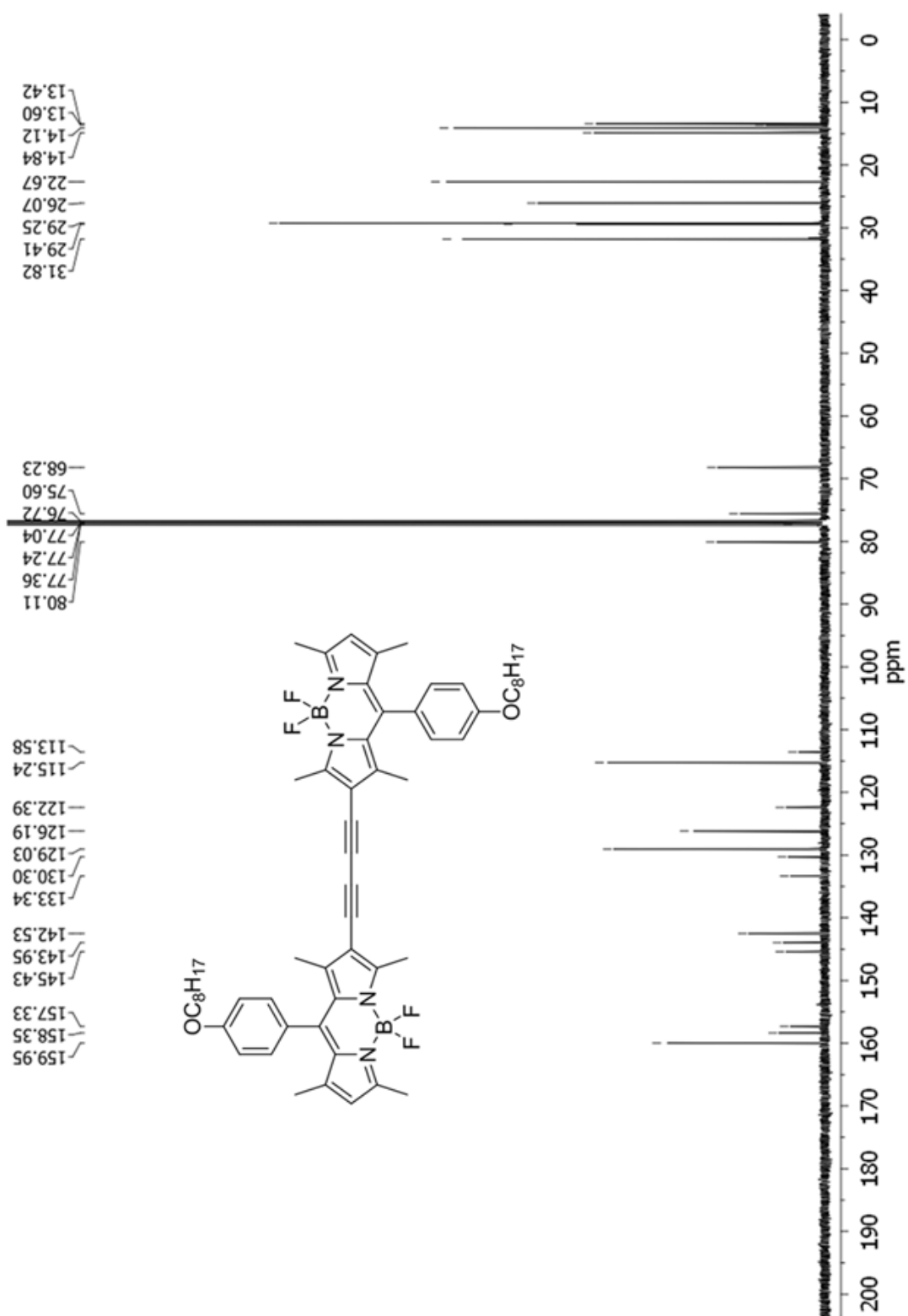


Figure S8. ^{13}C NMR spectrum of 4

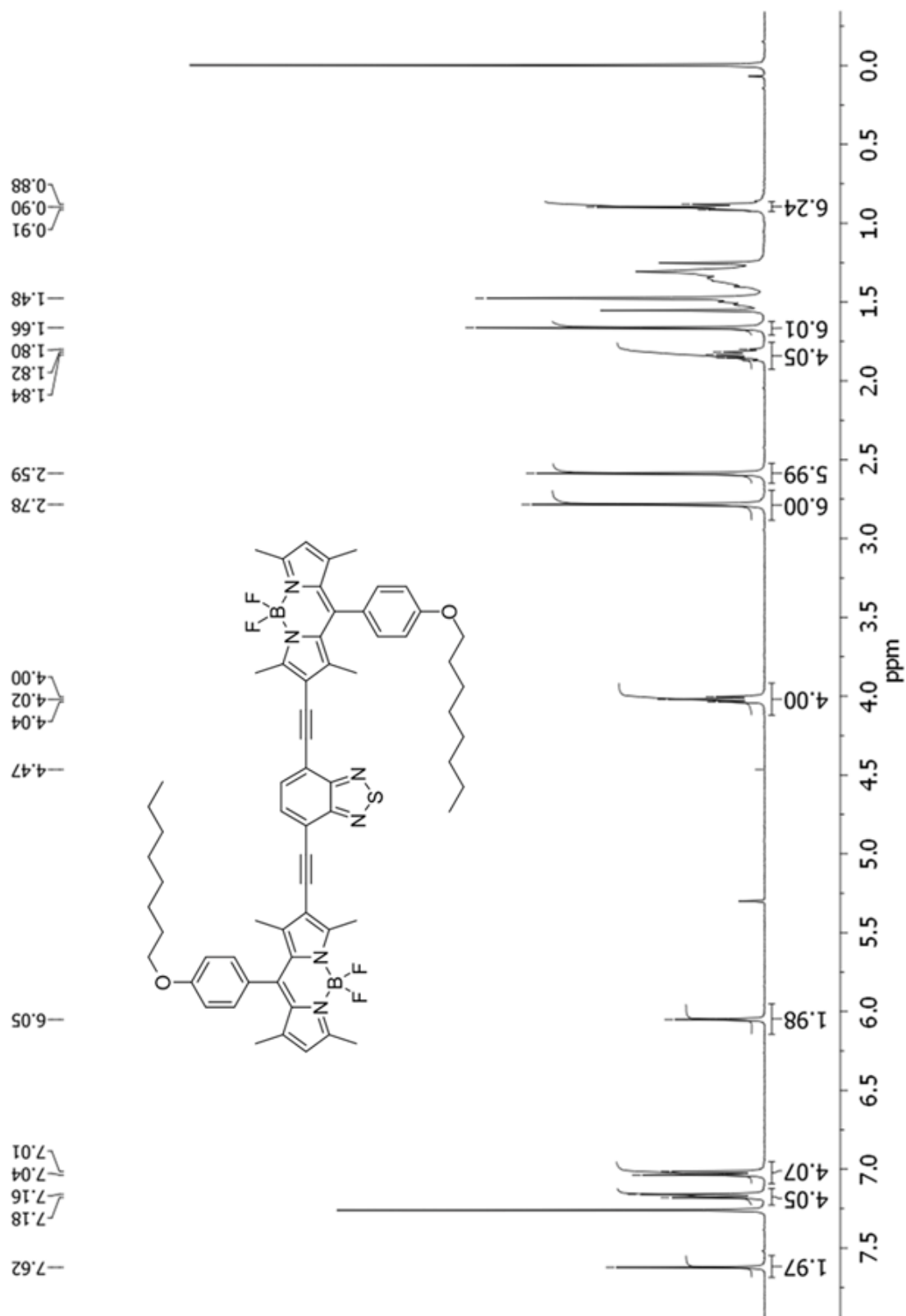


Figure S9. ^1H NMR spectrum of 3

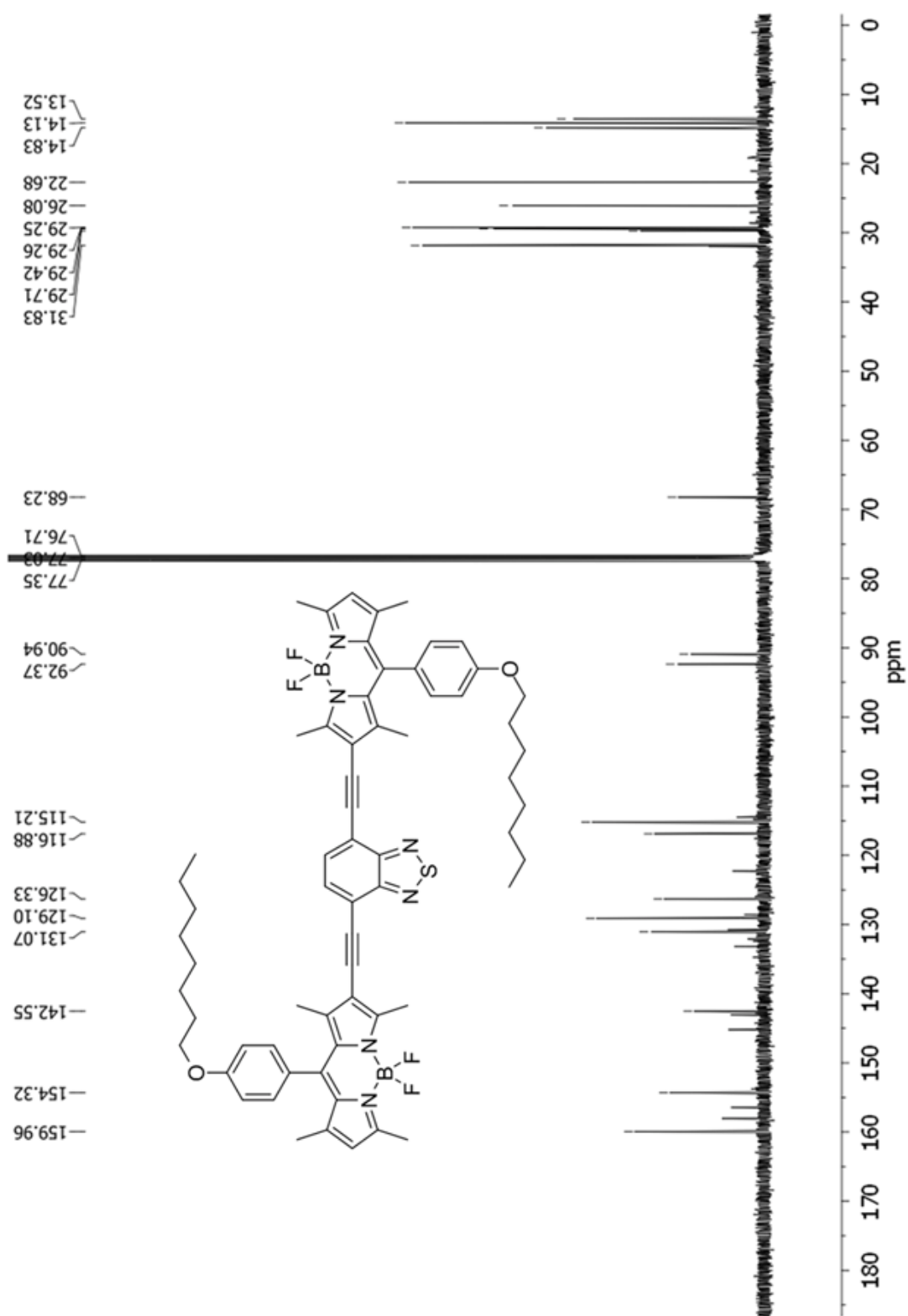


Figure S10. ^{13}C NMR spectrum of 3

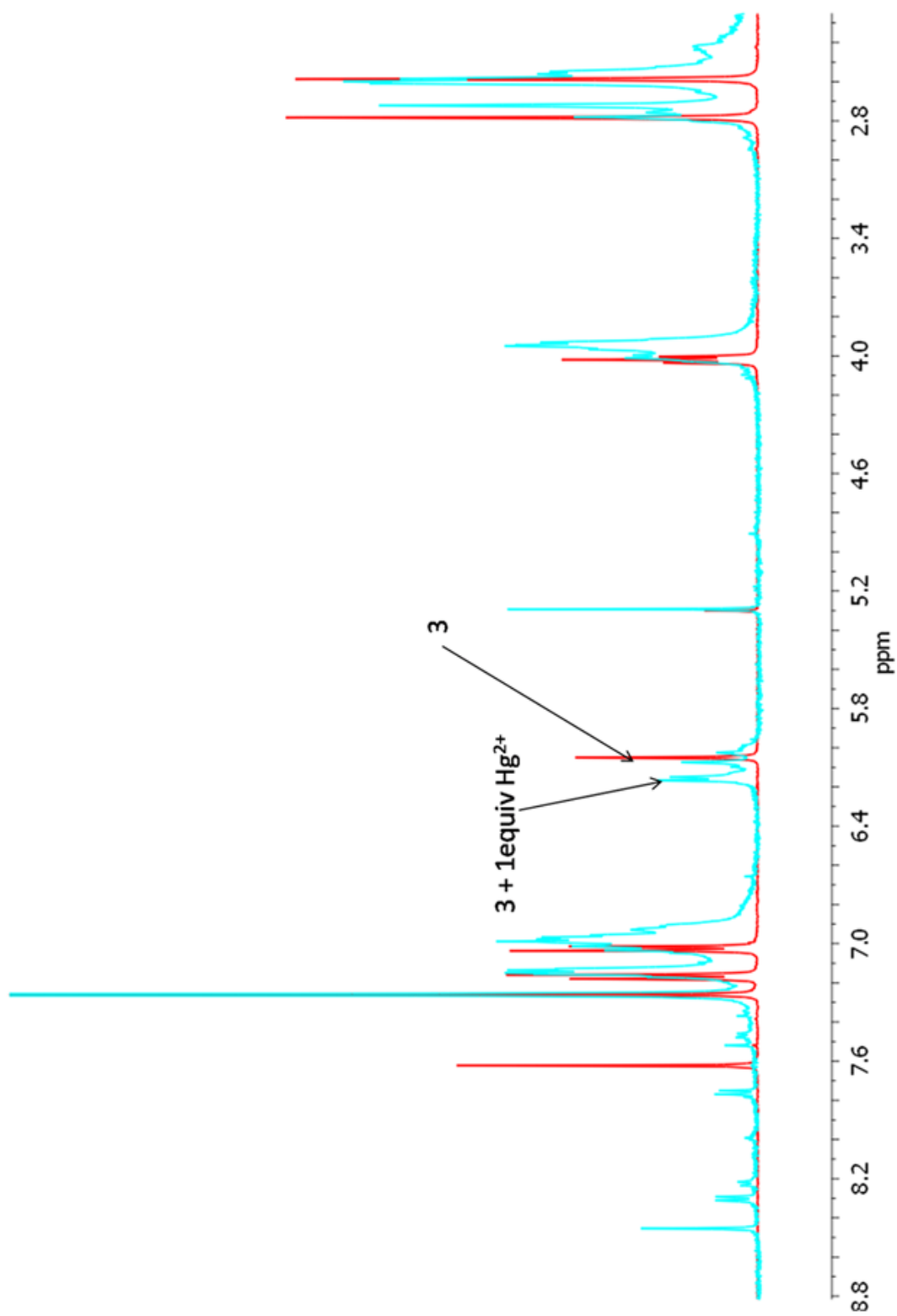


Figure S11. ¹H NMR spectrum of 3 and 3 with 1equiv Hg²⁺

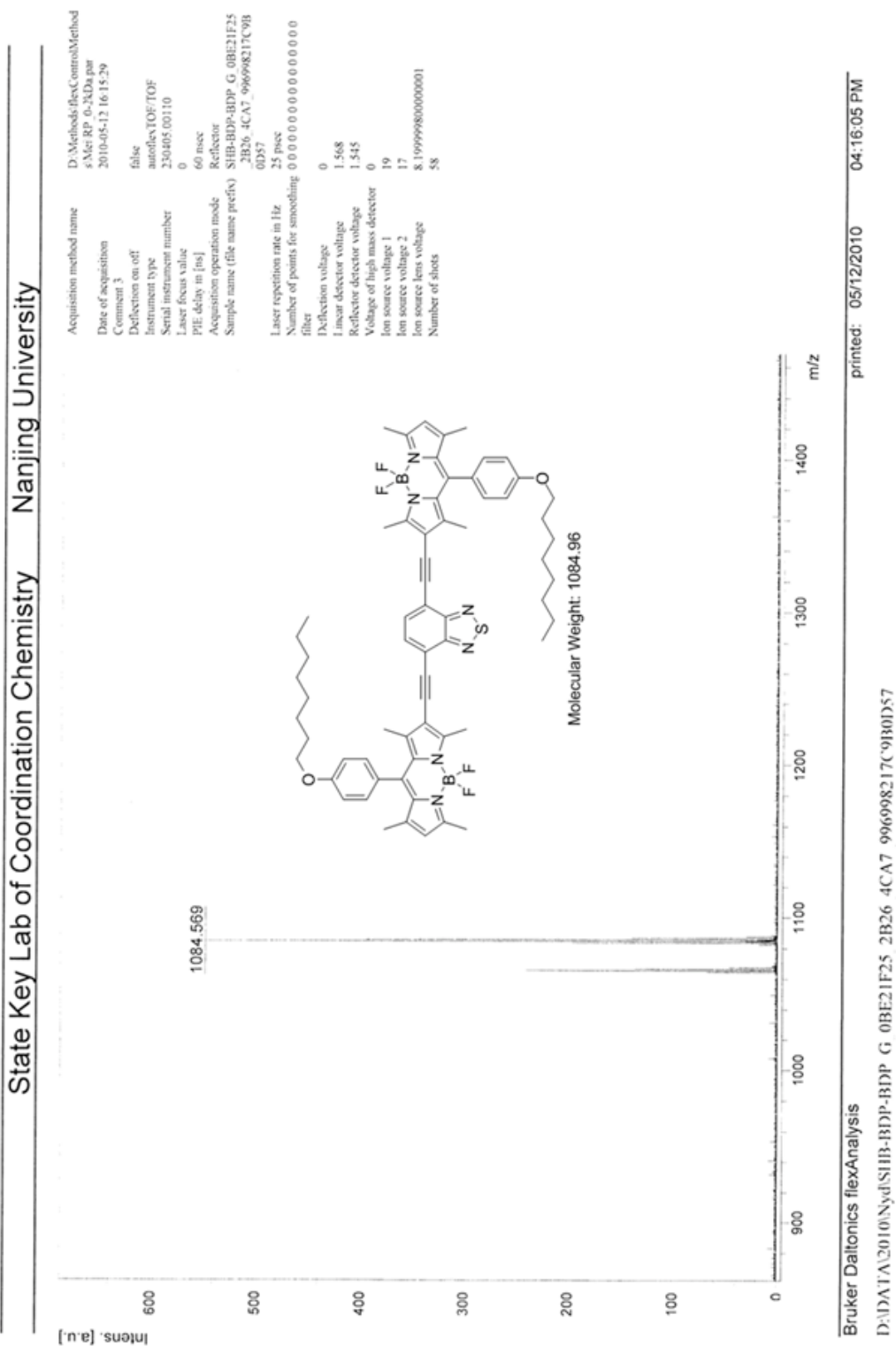
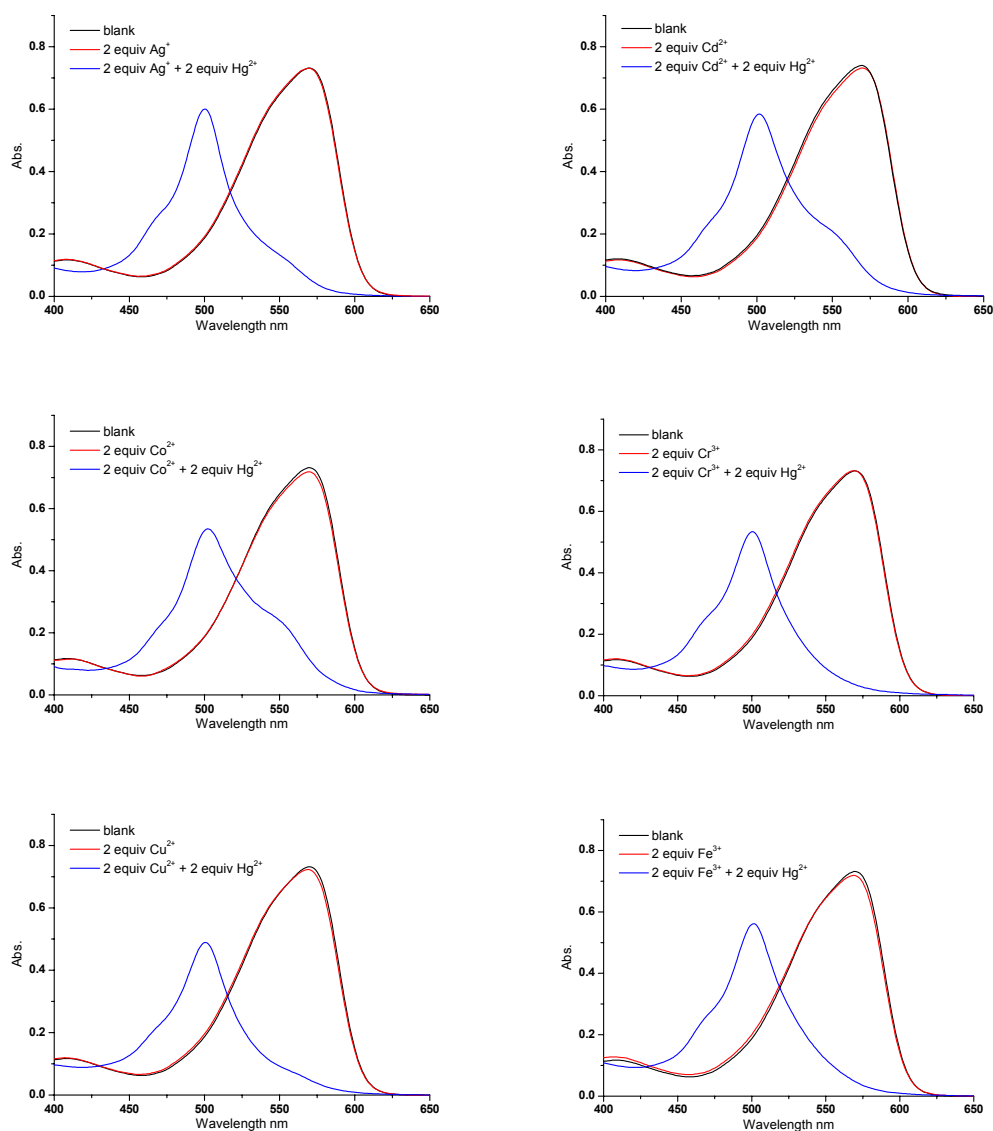


Figure S12. Mass spectra of 3

Figure S13. UV-vis spectroscopic titrations of 3 (1×10^{-5} M) with different metal ions (2×10^{-5} M) and the anti-interference ability



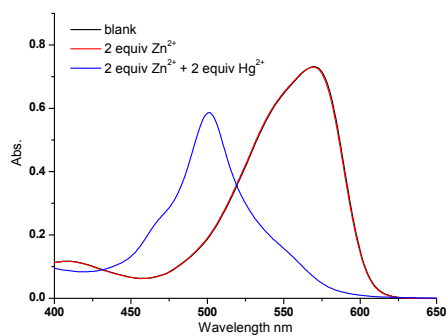
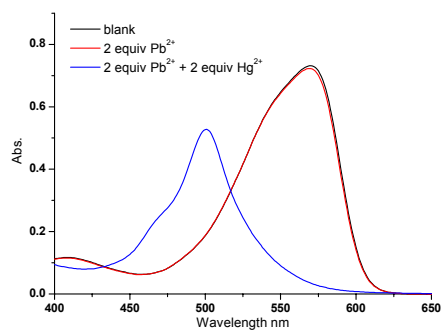
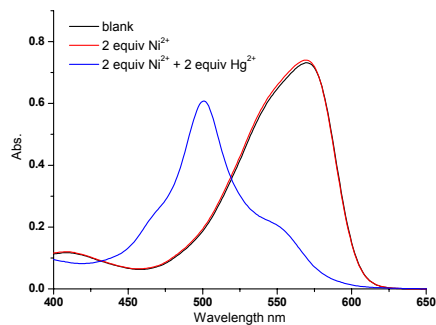
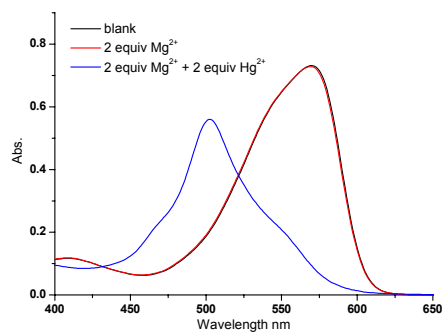
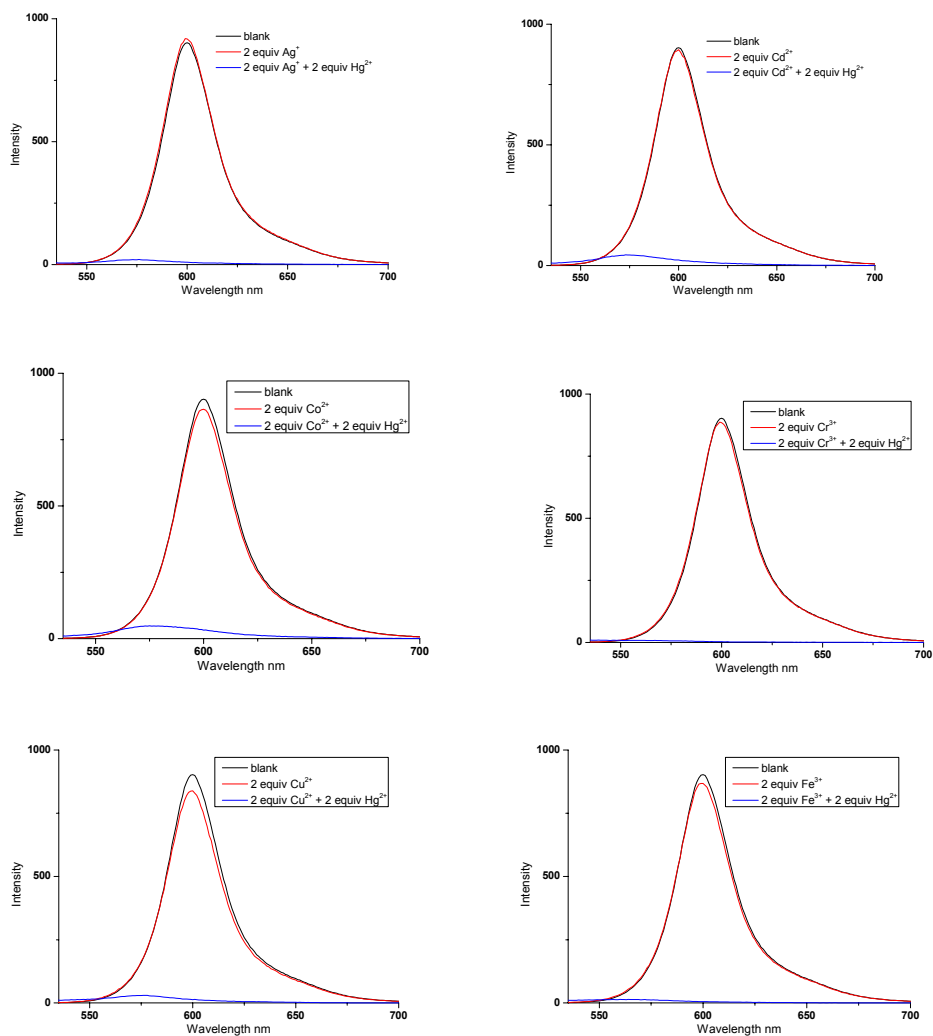


Figure S14. PL spectroscopic titrations of 3 (1×10^{-5} M) with different metal ions (2×10^{-5} M) and the anti-interference ability



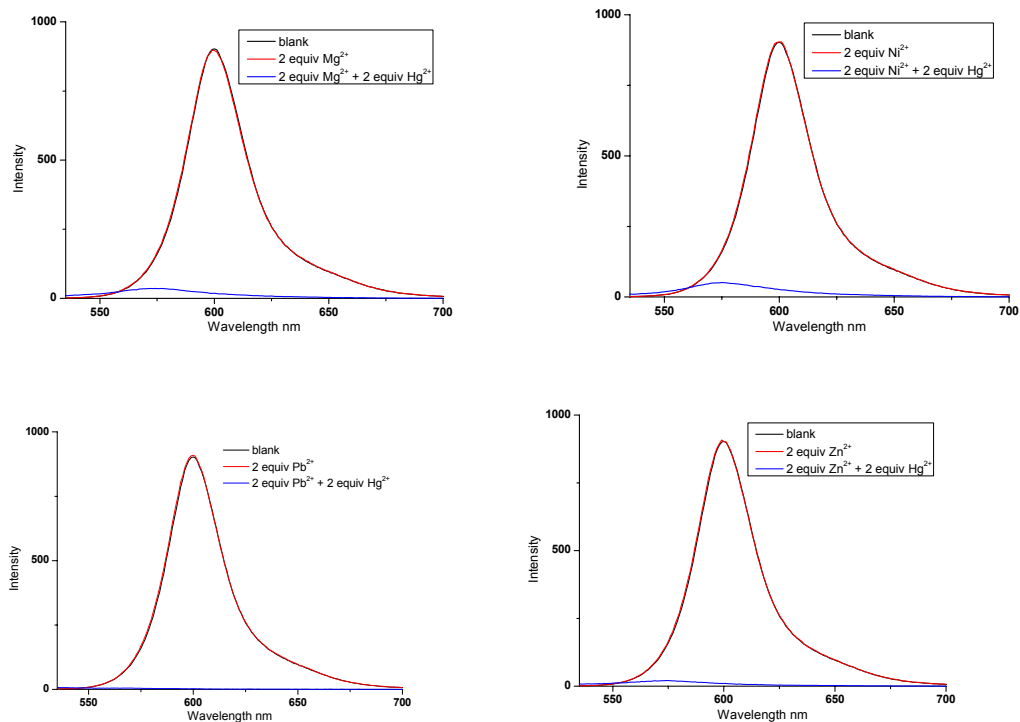


Figure S15. The dependence of both absorption and PL spectra of dye 3 on solvents

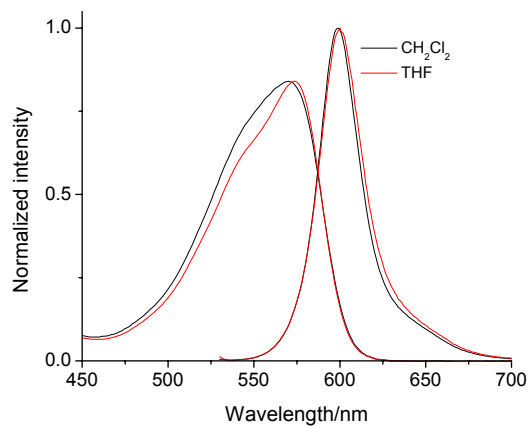


Figure S16. The absorption and emission spectra response of dye 4 to Hg^{2+}

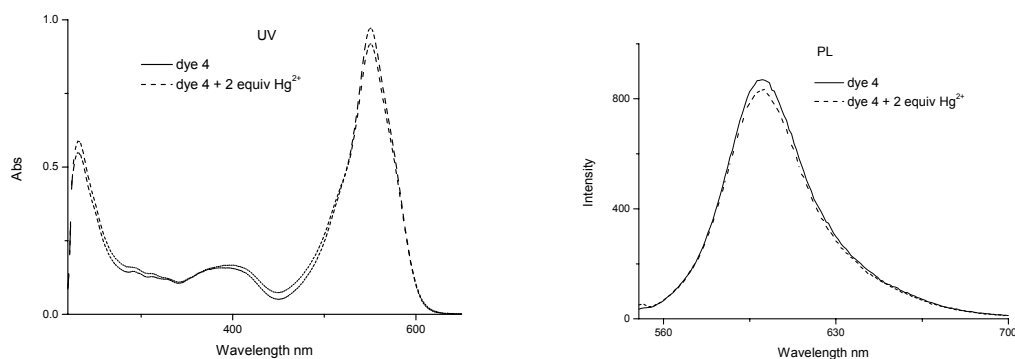


Figure S17. The cyclic voltammograms of dye 3, 4 and 3 in the presence of Hg^{2+} .

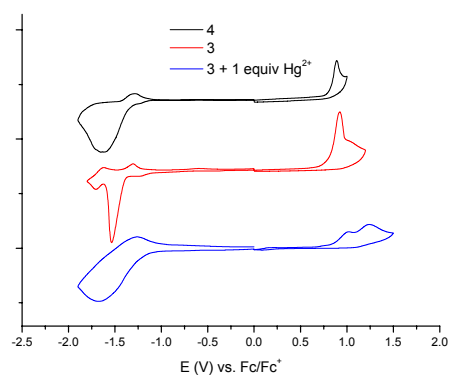


Figure S18. Reversibility test of probe 3 (1×10^{-5} M in CH_3CN)

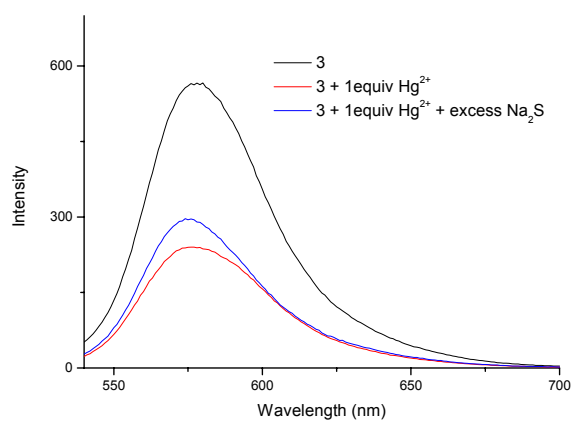
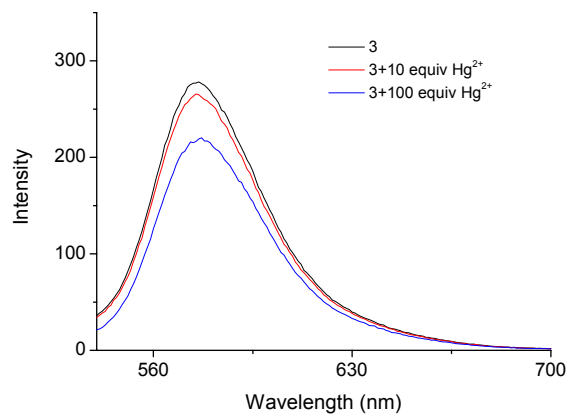


Figure S19. Detection performance of 3 in water system (THF:H₂O = 3:1, v:v, 2.5×10⁻⁶ M).



References

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